Application of Ion Cyclotron Resonance Spectroscopy to the Determination of Relative Hardness Scales for Ketones and Alcohols

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Summary An ion cyclotron resonance (i.c.r.) study has shown that gas phase hardness of dialkyl ketones and alkyl alcohols increases with increasing substitution, but decreases with decreasing ring size.

THE prediction of possible modes of organic reactions is often complicated by a variety of competing factors. The HSAB principle[1] has made it possible to correlate many complex phenomena,[2] and this principle can now be applied in a predictive sense. Acids and bases have at least two characteristic properties, *viz* strength, and hardness or softness,[3] and complexes of hard acids and bases or of soft acids and bases have an added stabilization.[4] Many recent reports[5,6] of the measurement of gas-phase acidity and basicity in particular systems have utilized i.c.r. spectroscopy, and we felt that it should be equally possible to use this technique to determine relative hardness or softness scales of organic bases in the gas-phase.

$$XY^+ + Z \longrightarrow XZ^+ + Y \qquad (1)$$

$$XZ^+ + Y \not\longrightarrow XY^+ + Z \qquad (2)$$

If we construct a system, described by reactions (1) and (2), in which the structures of the ions XZ^+ and XY^+ are chosen such that they are of an identical type, then enthalpy differences alone will determine the mode of reaction. If reaction (1) proceeds but reaction (2) does not, the implication is that there is an added stabilization for XZ^+ compared with XY^+. If X is hard, it follows from the HSAB principle that Z is harder than Y. By performing consecutive pairs of experiments it should be possible to construct relative hardness scales.

In this study we use the trimethylsilyl cation (from tetramethylsilane) as our hard Lewis acid (X) and its adduct formation with alcohols[7] or ketones[8] (which proceed with zero activation energy[8]) to produce XY^+ and XZ^+. The difference in electronegativity between silicon and carbon is 0·7; thus the electrophilic silicon centre should be hard. Evidence that alkylsilicon is indeed hard comes from solution chemistry; alcohols and alkoxides (hard) react at the silicon centre of acyloxysilanes, whereas organometallic reagents (soft) react at the carbonyl centre.[9]

The reaction of methanol (Y) and ethanol (Z) with Me_3Si^+ in the gas-phase provided the adducts $Me_3Si{-}\overset{+}{O}(Me)H$ (XY^+) and $Me_3Si{-}\overset{+}{O}(Et)H$ (XZ^+), respectively, using a Dynaspec I.C.R. 9 spectrometer, electron energy 70 eV, $\omega_c/2\pi = 124{\cdot}0$ kHz, ion transit time 2×10^{-3} s, and cell pressure 3×10^{-5} Torr [tetramethylsilane is maintained at 1×10^{-6} Torr, the pressures of the two alcohols (or ketones) are adjusted such that the two adducts show a 1 : 1 ratio of power absorbances and give a total pressure of 3×10^{-5} Torr]. Cyclotron ejection experiments were used to demonstrate[10] that reaction (3) occurred but that (4) did not.

$$Me_3Si{-}\overset{+}{O}(Me)H + EtOH \longrightarrow Me_3Si{-}\overset{+}{O}(Et)H + MeOH \qquad (3)$$

$$Me_3Si{-}\overset{+}{O}(Et)H + MeOH \not\longrightarrow Me_3Si{-}\overset{+}{O}(Me)H + EtOH \qquad (4)$$

As the trimethylsilicon centre is hard, and as ethanol displaces methanol from the adduct, it follows that ethanol is a harder base than methanol. This study was extended to include other alcohols and ketones and gave the following series of hardness scales and ionisation potentials[11] (eV): Bu^{t}COMe (9·2) > Pr^{i}COMe (9·3) > EtCOMe (9·5) > Me_2CO (9·7) = cycloheptanone (9·1) = cyclohexanone (9·15) > cyclopentanone (9·3) > cyclobutanone (9·4); Bu^{t}OH (9·9)[12] > Pr^{i}OH (10·1)[11] > cyclopentanol (9·95 ± 0·15)[13] = PrOH (10·2)[11] > EtOH (10·5)[11] > MeOH (10·8).[11]

Acyclic ketones follow the trend that as an alkyl group attached to the carbonyl carbon becomes more substituted, the carbonyl oxygen becomes harder. Cyclic ketones become softer bases as the ring size decreases. Alcohols follow a similar pattern, *i.e.* increased substitution on oxygen makes it a harder base. The position of cyclopentanol in this series was crucial since it allowed a distinction to be made between n-propanol and propan-2-ol.

The ionisation potentials (I.P.) of these molecules are a measure of the ability of the molecule to stabilize positive charge on oxygen, *i.e.* the lower the ionisation potential, the easier it is to stabilize the charge. Within congeneric series the hardness scale reflects the change in ionization potential, but a comparison of cyclic and non-cyclic compounds points to subtle steric or electronic differences between such compounds.†

For example, it would be expected that cyclopentanol (I.P. 9·95 eV) should displace propan-2-ol (10·1) from the adduct, but this was not observed. Cyclopentanol is equal in hardness to n-propanol (10·2). This dramatic effect also occurs for ketones, where cyclopentanone (9·3) will not displace acetone (9·7), but acetone and cyclohexanone (9·15) have the same hardness, and mutually displace each other. This demonstrates that caution must be exercised when using ionization potentials to describe a relative hardness scale within a particular series.

The technique described above allows the direct determination of the relative hardness of gas-phase bases.

We thank the Australian Research Grants Committee for financial support, and for the award of a postdoctoral fellowship to V.C.T.

(*Received*, 14*th November* 1978; *Com.* 1219.)

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† A referee has commented that in the case of cyclic and non-cyclic compounds the observed differences in ionisation potential could arise because the first ionisation potential may not always involve the oxygen lone pair.

[1] R. G. Pearson, 'Hard and Soft Acids and Bases,' Dowden, Hutchinson and Ross, Stroudsberg, Pa. 1973.

[2] Tse Lok Ho, *Chem. Rev.*, 1975, **75**, 1.

[3] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827.

[4] I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, London, 1976, p. 33—40.

[5] J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, 1977, **99**, 5417, and references cited therein.

[6] J. H. J. Dawson and K. R. Jennings, *Internat. J. Mass Spectrom. Ion Phys.*, 1977, **25**, 47.

[7] I. A. Blair, J. H. Bowie, and G. Phillipou, *Austral. J. Chem.*, in the press.

[8] I. A. Blair and J. H. Bowie, *Austral. J. Chem.*, in the press.

[9] P. F. Hudrlik and R. Feasley, *Tetrahedron Letters*, 1972, 1781.

[10] J. H. Bowie and B. D. Williams, *Org. Mass Spectrom.*, 1975, **10**, 141.

[11] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionisation Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' NSRDS-NBS 26, U.S. Dept. of Commerce, 1969.

[12] L. S. Levitt and B. W. Levitt, *Chem. and Ind.*, 1970, **73**, 990.

[13] Ionisation potential measured using the semi-log plot method (F.P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, 1951, **19**, 1254) with the I.C.R. 9 and krypton as standard.